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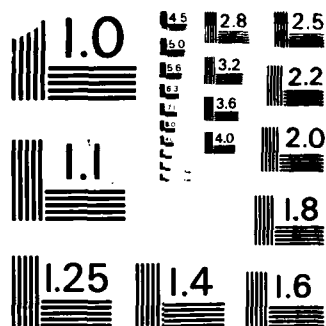
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REDISTRIBUTION OF ARSENIC IN SILICON
DURING HIGH PRESSURE THERMAL OXIDATION

by

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**REDISTRIBUTION OF ARSENIC IN SILICON
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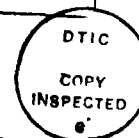
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The redistribution of arsenic in Si has been studied in terms of the relative rates of oxidation and diffusion in silicon. Redistribution of arsenic in silicon during oxidation is dependent on the ratio of oxidation rate to the diffusivity in silicon, $B/D^{1/2}$, as well as on the thermodynamic equilibrium segregation coefficient. It was found that for the value of $B/D^{1/2}$ larger than 50, most of the arsenic impurity becomes trapped in SiO_2 . For the smaller value of $B/D^{1/2}$, snowplowing of arsenic results.

The study of arsenic redistribution in silicon during thermal oxidation is important in the fabrication of shallow p-n junctions. Arsenic "snowplowing" at the Si-SiO₂ interface during 1 atm thermal oxidation of ion implanted Si has been described.^{1,2} In this paper, we report the redistribution of arsenic in silicon during 1 atm. HCl oxidation and also high pressure dry O₂ oxidation. The redistribution phenomenon has been investigated in terms of the ratio of the rates of oxidation of Si and diffusion of As in Si, $B/D^{1/2}$. When the oxidation rate is controlled by diffusion of oxygen through the existing oxide, the oxide thickness, X , will be given by:

$$X = Bt^{1/2} \quad (1)$$

where B is the parabolic growth rate constant at a given temperature for an oxidation time t . D is related to the As diffusion length X_{As} by:

$$X_{As} = 2 (Dt)^{1/2} \quad (2)$$

where D is the diffusivity of As in Si during time t . The ratio of the Si-SiO₂ interface velocity (dX/dt) to arsenic diffusion velocity (dX_{As}/dt), $B/(2D^{1/2})$, is a dimensionless quantity.

Samples were prepared by implantation of 25 keV, 3×10^{15} As⁺/cm², on (100), n-type silicon. High pressure, dry O₂ oxidations at temperatures of 600°C and 800°C have been made. Ramping up of the temperature of the high pressure apparatus to achieve thermal equilibrium, and ramping down after depressurizing was carried out in a nitrogen atmosphere. Oxygen pressures of 560 psi(38atm) up to 2100 psi(143 atm) were employed in order to change the oxidation rates, while keeping the diffusivity of arsenic constant. The high pressure apparatus and detailed procedures will be reported elsewhere, but are similar to previously published experiments.³ Normal 1 atm dry oxidation with a 4.5% HCl ambient at 600°C and 800°C was performed in order to change the relative rate by varying the temperature. The HCl ambient was introduced for impurity gettering.

All the samples were cleaned prior to oxidation by the RCA cleaning method⁴

followed by an 5 sec HF dip. The oxide thicknesses were measured by Nanospec/AFT 010-0180 and an ellipsometer. The depth profile of arsenic was examined by secondary ion-mass spectroscopy (SIMS) using a 15 keV primary O_2^+ beam and by 2 MeV He ion Rutherford backscattering spectroscopy (RBS). About 200 Å of gold was evaporated on the SiO_2 surfaces of the several samples in order to avoid charging of the SiO_2 during SIMS measurements. The ratio of the arsenic signal to the sputtered oxygen signal was used to improve quantitative accuracy of arsenic concentration measurements. Calibration of the arsenic concentration in the SiO_2 was made by using a standard sample which was prepared by implanting 100 keV, $1 \times 10^{15} \text{ As}^+/\text{cm}^2$ into 1500 Å thermal SiO_2 on Si.

When silicon is thermally oxidized, the dopant will redistribute at the interface until its chemical potential becomes equal on both sides of the interface, i.e., in Si and SiO_2 . The ratio of the thermodynamic equilibrium concentration of the impurity dopant in silicon to that in silicon dioxide at the interface is defined as the equilibrium segregation coefficient, m . The experimentally determined segregation coefficient may differ from the calculated thermodynamic equilibrium segregation coefficient^{5,6}. This is due to the competitive relationship between oxidation rate which releases impurities and the diffusivity of impurity, i.e., the rate at which one system achieves equilibrium. The pile-up and depletion phenomenon of impurities near the Si- SiO_2 interface is known to be dependent on the relative rates of oxidation and impurity diffusion in silicon and the segregation coefficient.^{5,8} Here, the relative rate is given by $B/D^{1/2}$ and the thermodynamic equilibrium segregation coefficient depends upon the ratio of the impurity solubility in the oxide to that in silicon. When the impurity segregation coefficient is less than 1 (higher solubility in the SiO_2 than in Si), as is the case for boron, the impurity will deplete into the SiO_2 .^{5,7} On the other hand, for the impurity segregation coefficient larger than 1, impurities such as arsenic will pile-up in Si near the interface as the Si surface recedes during oxidation. Hence, impurity pile-up or

depletion can be observed due to solubility differences between two phases regardless of impurity capture by the new product phase SiO_2 , or push-back into the Si by the SiO_2 . The relationship between the relative rate of oxidation to diffusion in silicon, $B/D^{1/2}$, and the impurity pile-up in Si or depletion into the SiO_2 near the Si- SiO_2 interface has already been observed before for both phosphorous and boron in Si.⁸ The redistribution of phosphorous in silicon for values of $B/D^{1/2}$ ranging from 0.1 to 10 was presented, with more pile-up found at the interface for greater values of $B/D^{1/2}$. Impurity "snowplowing" also depends on the diffusivity of the impurity in the oxide. For example, for impurities such as gallium in Si, there is no snowplowing, only depletion of Ga near the Si side of the interface due to fast diffusion of Ga in the oxide even though the segregation coefficient is larger than 1.⁵

During high pressure oxidation, the increased oxygen pressure enhances the oxidation rate significantly.^{9,10} When the oxidation rate is very high compared to the diffusivity of As in Si, trapping of As in SiO_2 is observed. For the low temperature 600°C oxidations at normal 1 atm or at elevated pressure, the oxidation rate becomes significantly greater than the diffusion rate of arsenic, which is relatively unaffected by the O_2 pressure. This is due to the fact that the diffusivity value decreases more rapidly with temperature than the oxidation rate. Figure 1 shows the As and O profiles in the SiO_2 on Si sample for 1520 psi O_2 oxidation at 600°C for 5 min. Trapping of the arsenic in SiO_2 is clearly observed in Figs. 1 and 2. It has been confirmed by RBS and SIMS that the amount of arsenic trapped in SiO_2 is greater for oxidation at 1520 psi than those for 970 psi, at 800°C and 5 min oxidation. It reduces further for 560 psi at 800°C for 5 min oxidation (Fig. 3) and the trapping is totally insignificant for 1 atm (or 14.7 psi) at 800°C for 6 hours oxidation (Fig. 4). A slight pile-up in silicon near the interface is attributed to the effect of arsenic solubility differences between the Si and the SiO_2 phases (Fig. 1, 2). On the other hand, "snowplowing" of arsenic is observed in Fig. 3 for 560 psi, 5 min at 800°C, and most pronounced for 1 atm. at 800°C, 5 min. oxidation (Fig. 4). From a

concentration dependent diffusivity calculation¹¹ and for a 1 atm oxidation at 800°C, $X_d = 2(Dt)^{1/2}$, the diffusion length $X_d = 2(Dt)^{1/2}$ of arsenic is about 360Å. Considering the molar ratios, the depth of Si consumed for 2000Å of oxide growth will be 880 Å ($d_{Si} = 0.44d$, where d is thickness of SiO₂). Arsenic snowplowing is shown in Figs. 3, 4. Arsenic snowplowing in Si near the interface is likely due to the impurity segregation coefficient, rather than impurity diffusion. These results reveals two aspects of the redistribution phenomena depending on the conditions. One is that the thermodynamic equilibrium segregation coefficient dominates when the diffusion rate is high enough; the other is that the oxidation rate dominates over the thermodynamic equilibrium segregation coefficient for the low temperature, or high pressure condition.

In Table 1 below, the ratio of the rates of oxidation and dopant diffusivity in silicon, $B/D^{1/2}$ for our experimental conditions, are given. For an oxide thickness less than 1000Å (including high pressure oxidation), oxidation time and thickness were extrapolated (using $\log x$ versus $\log t$) into the possible parabolic growth region for obtaining the dimensionless quantity, $B/D^{1/2}$. Arsenic diffusivity values for 800°C and 600°C were extrapolated from the diffusivity graph.¹¹ As our calculations indicate, snowplowing of the arsenic impurity results for $B/D^{1/2}$ smaller than 50. The amounts of arsenic in the SiO₂ increases with increasing $B/D^{1/2}$. In the case where $B/D^{1/2}$ exceeds 50, the Si-SiO₂ interface advancement becomes dominant over the thermodynamic segregation coefficient, hence no snowplowing occurs and most of the arsenic becomes trapped. Deal observed that an impurity such as phosphorous accumulates more in Si near the interface for $B/D^{1/2}$ ranging from 0.1 to 10, as the temperature becomes lower or the $B/D^{1/2}$ ratio increases.^{8,12}

These observations indicate a strong dependency upon the relative rates $B/D^{1/2}$ of arsenic impurity pile-up, trapping phenomena during thermal oxidation. For the $B/D^{1/2}$ value larger than 50, the oxidation rate dominates, producing predominant non-

equilibrium conditions. The pile-up beyond this critical value is complicated and depends both upon the relative rates $B/D^{1/2}$ and chemical potentials. The thermodynamic equilibrium segregation coefficient becomes dominant for $B/D^{1/2}$ ranging from 50 downwards.

In conclusion, the redistribution of As during thermal oxidation of Si depends on the ratio $B/D^{1/2}$. Dominance of the oxidation rate over other factors, such as the thermodynamic equilibrium segregation coefficient and diffusion rate, has been observed. For $B/D^{1/2}$ larger than the order of 50, arsenic atoms are trapped in the SiO_2 . For $B/D^{1/2}$ below 50, arsenic snowplowing results, which means a dominance of thermodynamic segregation coefficient over the oxidation rate.

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Figure Captions

Figure 1

A SIMS profile of arsenic in SiO_2 grown on 25 KeV, $3 \times 10^{15} \text{ As}^+/\text{cm}^2$ I/I Si substrate at 600°C , 1520psi, 270 min with dry O_2 ambient. 200 Å gold film has been evaporated on SiO_2 .

Figure 2

A large amount of arsenic was trapped in the SiO_2 during 1520 psi, 5 min dry O_2 oxidation at 800°C .

Figure 3

A significantly reduced arsenic trapped in the SiO_2 , compared with results for oxidation at higher $B/D^{\frac{1}{2}}$ values, has been observed while arsenic snowplowing has also been seen.

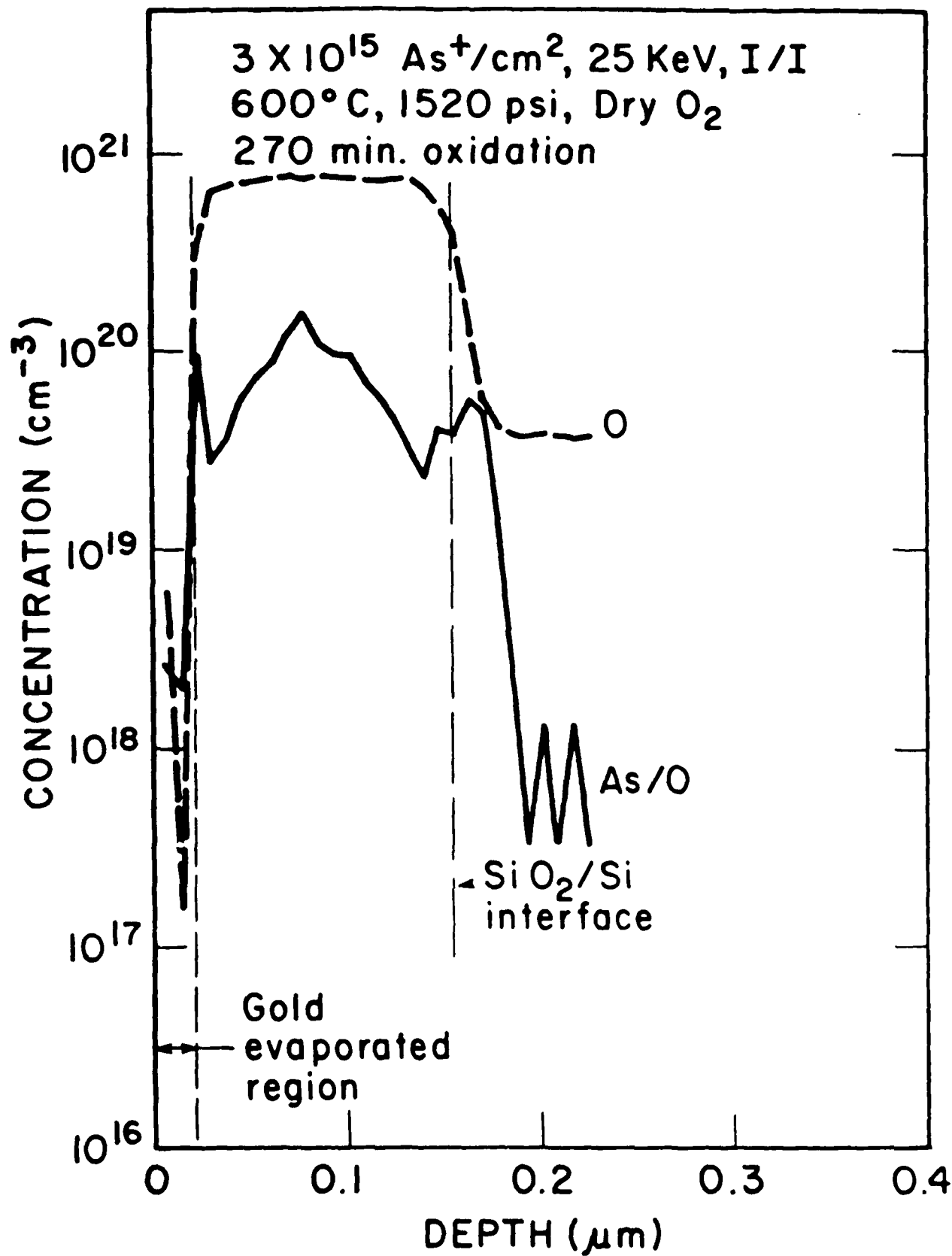
Figure 4

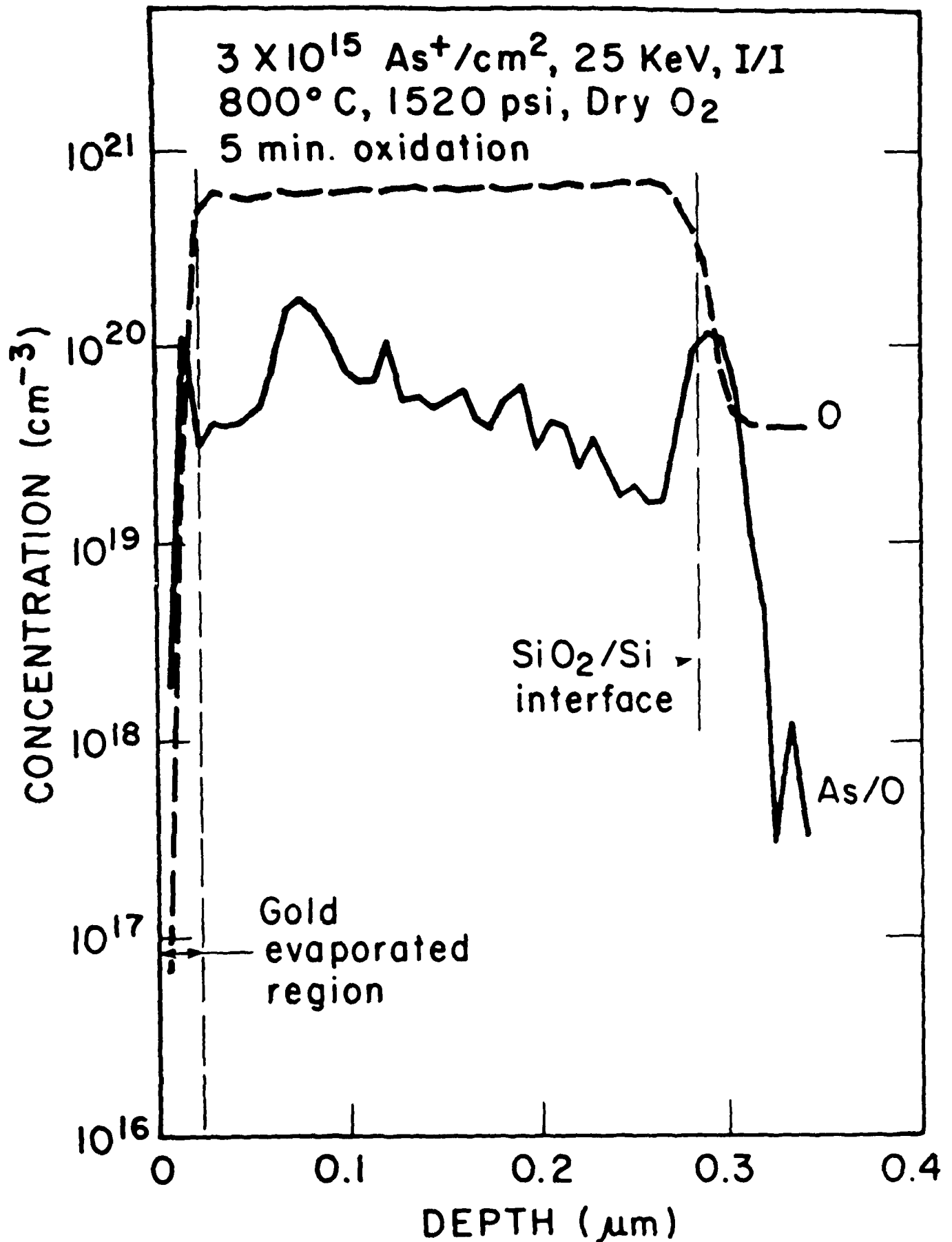
A prominent arsenic snowplowing has been observed for the $B/D^{\frac{1}{2}}$ value of 10.

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Fig 1a

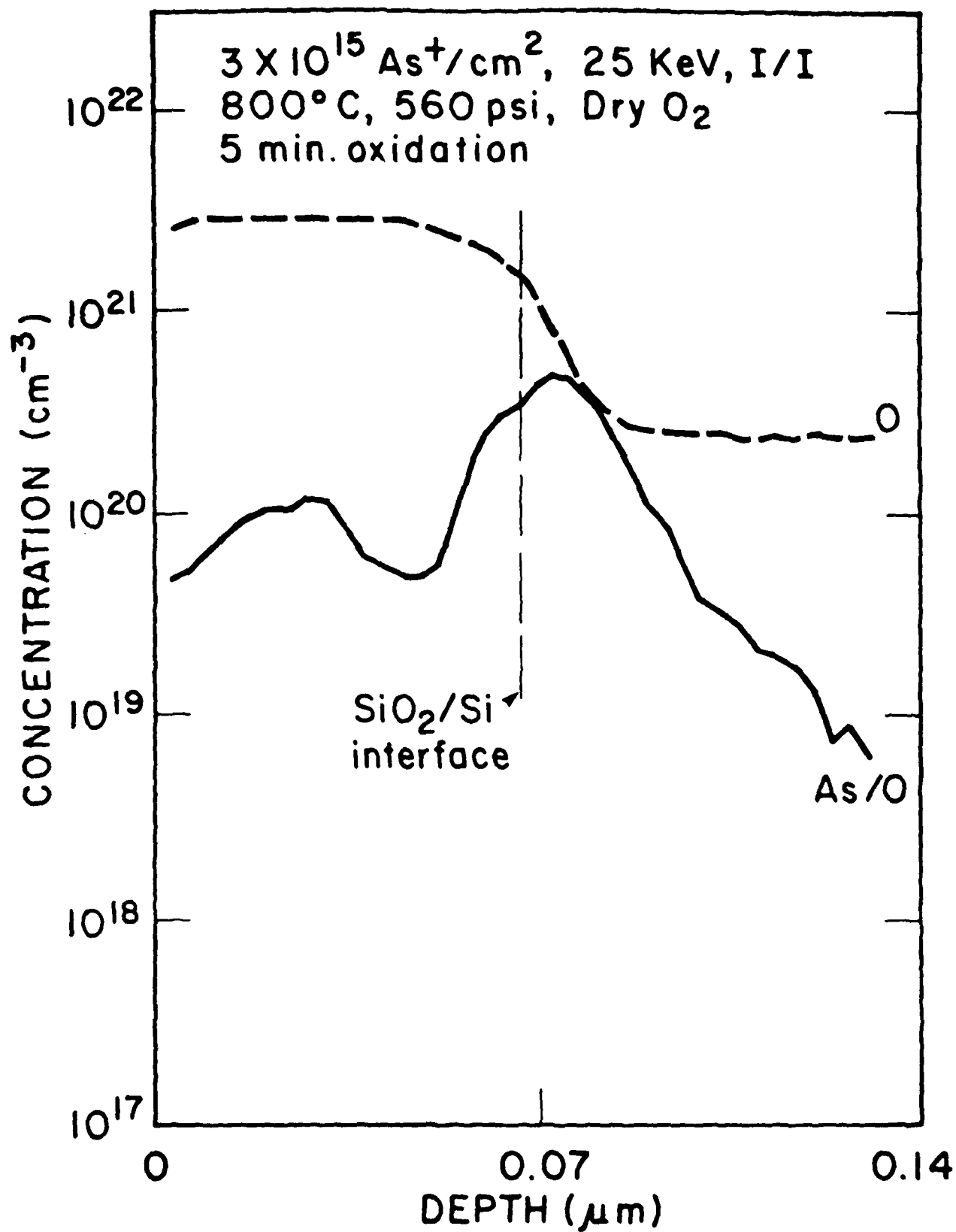


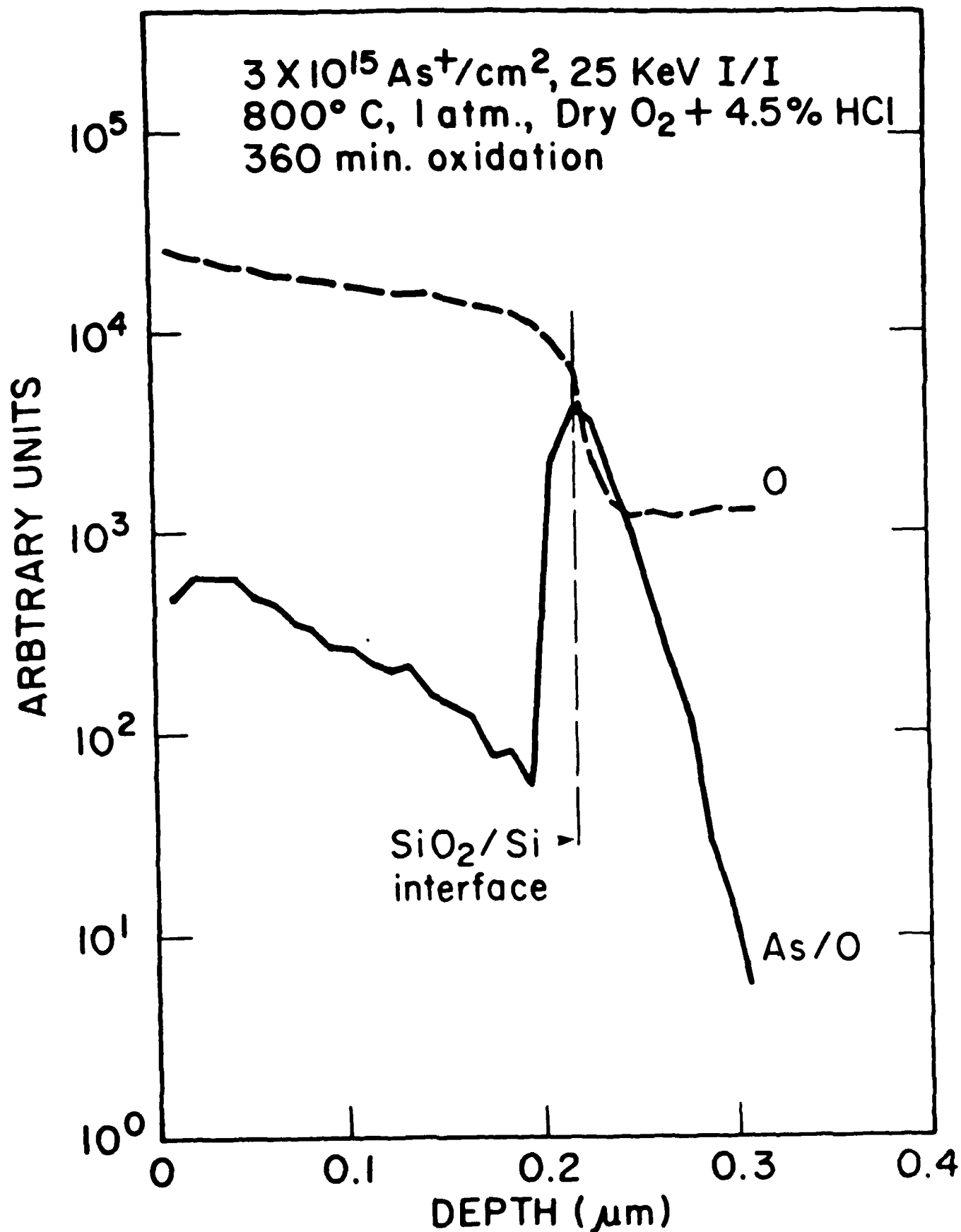


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Fig. 3/4





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